Characterization, Sources and Sinks of Colored Detrital Matter in the Ocean

Ralf Goericke

Marine Life Research Group
Scripps Institution of Oceanography
La Jolla, CA 93093-0218
phone: (619) 534-7970 fax: (619) 534-6500 email: rgoericke@ucsd.edu
Award #: N000149810005

LONG-TERM GOALS

My primary research interest is the effect that phytoplankton community structure has on the optical fields and carbon cycling in the marine environment. Methods used in my lab are based on biomarkers, primarily chlorophylls, carotenoids and their degradation products. These are the chromophores which are responsible for a major fraction of the light absorbed in the ocean. It is my goal to characterize phytoplankton-derived chromophores in the marine environment and determine their effects on ocean optics and access their utility as biomarkers for the study of phytoplankton and processes associated with these in the ocean.

OBJECTIVES

The optical properties of the ocean are primarily determined by the optical properties of water, particles and dissolved matter. The absorption of light by particles is due to phytoplankton, colored detrital matter (CDetM) and minerals. Whereas the chromophores associated with phytoplankton have been studied extensively over the last 50 years, little is known about chromophores associated with CDetM, even though these can contribute significantly to the absorption of light in the coastal zone. This project is a study of the nature and the sources and sinks of CDetM in the water column. The study's objectives were:

1. Characterize the chromophores of different classes of detrital matter, i.e., fresh and partially degraded fecal matter, resuspended sediments, particulate matter from below the euphotic zone and living organisms devoid of phytoplankton-derived pigments.
2. Search for specific chromophores that uniquely identify the different classes of detrital matter such that these marker-chromophores can be used to identify contributions of different classes of detrital matter to CDetM in the upper ocean.
3. Develop methods for the routine analysis and characterization of CDetM.
4. Determine photo-degradation rates and microbial-degradation rates of different detrital chromophores in order to understand the dynamics of these compounds in the upper ocean.

APPROACH

As potential sources of CDetM, phytoplankton, zooplankton, sediments and fecal material is subjected to chemical tests to identify and characterize the major chromophores associated with these. To characterize sinks, selected material is subjected to controlled microbial degradation and photooxidation. These experiments delineate the relevant time scales for these compounds in the water column as a function of temperature and light. Methods used to determine the relative contributions of

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phytoplankton, detrital chromophores and minerals to the absorption of light by particles in the ocean are tested using mixtures of phytoplankton and high- and low-carbon sediments.

WORK COMPLETED

I developed a method for the analysis of phytoplankton pigments and their degradation products in fecal matter and sediments and used this method to inventory chlorins (chlorophylls and their degradation products) in fecal matter and sediments (Goericke et al., in prep.a; in prep.b). I completed work on carotenol-chlorin esters and on the characterization and distribution of cyclic pheophorbides (Goericke et al.,1999; 2000a). I developed and tested sequential extraction methods for the partitioning of particulate absorption between phytoplankton, detrital chromophores and minerals. I performed microbial degradation experiments to determine the stability of chlorins and in particular cyclic pheophorbides in oxic and anoxic environments. I characterized the pigment complement of *Prochlorococcus marinus* found in at the top of the oxygen minimum zone in the Eastern Tropical North Pacific and the Arabian Sea (Goericke et al., 2000b). In collaboration with the group of Dan Repeta we began a study of nitrogen isotopic fractionation in algae and the development of methods for the isolation of Chl a for stable isotope analyses (Sachs et al., 1999).

RESULTS

We recently discovered a new class of Chl *a* degradation products, carotenol chlorin esters (CCEs) in sediments and water column particulate matter. Chlorins associated with these were identified as pheophorbide *a* and pyropheophorbide *a*. The carotenols are isofucoxanthin-5'-dehydrate and isofucoxanthinol-5'-dehydrate, compounds uniquely derived from fucoxanthin, a biomarker for diatoms. CCEs were only found in the fecal matter of copepods grazing on diatoms, not in fecal matter of microzooplankton grazing on flagellates. Based on these results it is hypothesized that CCEs are a sedimentary biomarker for diatoms.

The pigment 13^2, 17^3-cyclopheophorbide *a* enol (CCPA516) has only recently been discovered in marine sediments, where it contributes up to 60% to all solvent extractable Chl *a* degradation products. An analytical system for its quantification in sediments was developed and used to discover a series of cyclic pheophorbides based on divinyl chlorophylls *a* and *b* and on chlorophylls c_1 and c_2. It was shown that even though CPPA516 is very labile in organic solvents it is fairly stable when associated with sedimentary particles that are suspended in oxygenated seawater. It is probable that CPPA517 associated with sediments is stabilized by complexation with metals. CPPA516 is produced by all marine herbivores we have studied to date, i.e., diverse protozoans, the copepod *Calanus pacificus*, the euphausid *Euphausia* sp. and salps.

Results of microbial degradation experiments with sediments under oxic and anoxic conditions suggest that degradation of detrital chromophores is negligible on a time scale of tens of days, the time scale of resuspended sediments in the water column. It is noteworthy, that this result also applies to cyclic pheophorbides which are extremely labile in solutions of organic solvents. It is likely that the keto-enol system, which is highly susceptible to oxidation, is stabilized in aquatic systems by metal ions.

The marine cyanobacterium *Prochlorococcus marinus* contributes significantly to phytoplankton biomass and primary production in the subtropical and tropical open ocean. Its major pigments were characterized previously, its minor pigments were characterized as part of this project. The chl c-like pigment found previously in *Prochlorococcus* was identified as 2, 4 divinyl Mg-pheoporphyrin a_5

methyl ester. I found in populations of Prochlorococcus from the upper portion of the oxygen minimum zones of the Eastern Tropical North Pacific (ETNP) and the Arabian Sea high concentrations of parasiloxanthin (7',8'-dihydro-zeaxanthin), a pigment previously only found in the Common Japanese Catfish, rather than zeaxanthin. Analysis of water column and sediment trap particulate matter and sediments from the ETNP revealed substantial contributions of Divinyl-Chl a derived Chlorins to total chlorins in this environment, suggesting that Prochlorococcus, and by implication picoautotrophs, contribute significantly to export fluxes in this environment. It is likely that the microbial loop is 'short-circuited' in this environment by salps.

Tests with phytoplankton, extremely carbon-rich sediments from the Peru margin and extremely low-carbon sediments from the deep oligotrophic ocean demonstrated that currently used methods for the measurement of phytoplankton and detrital contributions to the absorption of light in the ocean are inadequate. These tend to overestimate the contribution of phytoplankton when concentrations of organic detrital chromophores are high. We have begun to develop an alternative method to determine relative contributions of phytoplankton, detrital chromophores and minerals to the absorption of light in the ocean. Initial tests are very promising.

IMPACT/APPLICATIONS

The work performed to date impacts on currently used methods to measure Chl *a* degradation products in the ocean, methods used to partition the absorption of light by particles between phytoplankton and detrital contributions and it changes our view of Chl a diagenesis in the water column and in sediments. The discovery of high concentrations of non-fluorescent cyclic pheophorbides in fecal matter suggests that the concept of 'pheopigments', as defined by analytical methods based on fluorescent detection, is inadequate. Complete quantification of Chl *a* degradation products requires chromatographic methods. Methods used to partition particulate absorption between phytoplankton and detritus overestimate the contribution of phytoplankton. These methods need to be improved. Current paradigms of chlorophyll diagenesis in recent and ancient sediments suggest that the structural diversity of porphyrins in ancient sediments is set by redox conditions in the sediment. However, structural considerations suggest that the structural diversity of sedimentary porphyrins may be set by rates of cyclic pheophorbide production relative to rates of pheophorbide/pheophytin production. Or restated, the structural diversity of porphyrins found in ancient sediments may rather be due to the action of grazers in the water column, rather than diagenesis in the sediments.

RELATED PROJECTS

I have begun a detailed, NSF-funded study of carotenol-chlorin esters. The objectives are to prove the hypothesis that these are uniquely derived from the grazing of crustaceans on diatoms, to study the distribution of these in the marine environment and explore the stable isotope composition of these for paleoecological studies.

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